TITLE: Heat of Dissolution Measurements for CO_2 in Mixed Alkanolamine Solvents

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ABSTRACT

The main objective of this project is to measure heat of dissolution of CO_2 in carefully selected mixed alkanolamine solvent systems, and provide such directly measured data that might be used for efficient design of CO_2 capture processes, or for better understanding of thermodynamics of CO_2- alkanolamine systems. Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO_2, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. For more economical CO_2 capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO_2 in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 40 and 80C and various partial pressures of CO_2. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO_2 capture with potential for commercialization.

EXECUTIVE SUMMARY

The main objective of this project is to measure heat of dissolution of CO_2 in carefully selected mixed alkanolamine solvent systems, and provide such directly measured data that might be used for efficient design of CO_2 capture processes, or for better understanding of thermodynamics of CO_2- alkanolamine systems. Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO_2, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. For more economical CO_2 capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO_2 in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at temperatures 15, 40 and 80C and various partial pressures of CO_2. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO_2 capture with potential for commercialization.

Data measurements for CO_2 in aqueous MEA, MDEA and mixtures of MEA and MDEA were completed and reported previously. During the current period of performance, October 2005 to March 2006, data measurements for CO_2 in aqueous mixtures of MEA, MDEA and piperazine were initiated and are currently continuing. The results of these measurements will be reported during the next reporting period. Some data measurements are also being attempted using an inorganic fluorinated salt as an additive. The intent is to investigate if this additive alters the solvent properties favorably. There was a delay in measurements caused because the graduate student performing the experiments quit due to personal reasons. A new M.S. student has undertaken the measurements. Although it took over two months for this student to get familiar with the project, he has gained sufficient expertise to continue the measurements.

Some efforts are being made to extend the currently available thermodynamic models for these systems based on the electrolyte –NRTL/UNIQUAC activity coefficient correlations for enthalpy calculations. The approach involves development of EOS-G^E model with equations of state and mixing rules available in the literature.

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1. Introduction

Carbon dioxide is one of the major greenhouse gases, and the need for stabilization of its composition in earth's atmosphere is vital for the future of mankind. Although technologies are available for capture and storage of CO_2, these technologies are far too expensive for economical commercialization. Reduction of cost would require research for refinement of the technology. The idea of capturing CO_2 from the flue gas of power plants did not start with concern about the greenhouse effect. Rather, it gained attention as a possible economic source of CO_2 , especially for use in enhanced oil recovery operations where CO_2 is injected into oil reservoirs to increase the mobility of the oil and, therefore, the productivity of the reservoir. Several commercial CO_2 capture plants were constructed in the late 1970s and early 1980s in the US. The North American Chemical Plant in Trona, CA, which uses the carbonation of brine to produce CO_2 , started operation in 1978 and is still operating today. However, when the price of oil dropped in mid-1980s, the recovered CO_2 was too expensive for enhanced oil recovery operations and all of the other CO_2 capture plants were closed.

Historically, CO_2 capture processes have required significant amounts of energy, which reduces the power plant's net power output. For example, the output of a 500 MW (net) coal-fired power plant may be reduced to 400 MW (net) after CO_2 capture. This imposes an "energy penalty" of 20%. The energy penalties of current capture technologies range from about 30% for conventional coal to about 15% for advanced coal. It is desired that in the next decade these numbers be brought to 50% of their current values.

To date, all commercial CO_2 capture plants use processes based on chemical absorption with the monoethanolamine (MEA) solvent. MEA was developed over 60 years ago as a general, non-selective solvent to remove acid gases, such as CO_2 and H_2S, from natural gas streams. The process was modified to incorporate inhibitors to resist solvent degradation and equipment corrosion when applied to CO_2 capture from flue gas. Also, the solvent strength was kept relatively low, resulting in large equipment sizes and high regeneration energy requirements. The process allowed flue gas to contact an MEA solution in the absorber. The MEA selectively absorbed the CO_2 and was then sent to a stripper. In the stripper, the CO_2 –rich MEA solution was heated to release almost pure CO_2 . The lean MEA solution was then recycled to the absorber.

Other processes have been considered to capture CO_2 from the flue gas of a power plant, e.g., membrane separation, cryogenic fractionation, and adsorption using molecular sieves. These processes are even less efficient and more expensive than the chemical absorption. The reason can be attributed to the very low CO_2 partial pressure in the flue gas. Therefore, a high priority research need is to formulate new solvents that can significantly reduce the energy penalty associated with chemical absorption. The new solvents must increase the loading (amount of CO_2 dissolved per unit amount of solvent), and the rate of CO_2 dissolution while maintaining a low heat of solution, so as to minimize the energy requirements during the solvent regeneration.

For the processes based on the absorption of CO_2 by aqueous alkanolamines, the energy penalty or the cost of the process depends mostly on three factors: (1) the loading of CO_2 (moles of CO_2 absorbed per mole of amine), (2) the rate of CO_2 absorption, and (3) the energy requirement for the release of CO_2 in the stripper. For a number of solvents, detailed studies are available in the literature for the first two factors. Aqueous MEA solvents suffer from the limitation that CO_2 loading cannot exceed much higher than 0.5. An amine that is considered as a potential replacement for MEA is methyldiethanolamine (MDEA) because of the high loading of CO_2 (approaching 1) which is attributed to the stoichiometry of the reaction forming carbamate. However, the rate of CO_2 absorption by MDEA is too low for commercial applications. Mixed solvents containing MEA and MDEA, and diethanolamine (DEA) and MDEA in water seem to provide good solutions to give high absorption rates as well as CO_2 loading. Recently researchers have also started looking at other additives to aqueous MEA and MDEA mixtures to enhance solubility and rate of absorption of CO_2. These include sulfolane, N-methylpyrrolidone (NMP), and piperazine (PZ). Of these, piperazine seems to be the most effective in increasing the solubility of CO_2. The data available in the literature indicate that aqueous mixtures of MEA, MDEA and piperazine have potential to provide a solvent system superior to aqueous MEA solvent of the current commercial capture plants. However, a true determination of this is difficult without a detailed study of the relative energy requirements for each of the solvents. Such a study is not available in the literature, mostly because of lack of experimental data on the heats of dissolution of CO_2 in the aqueous alkanolamine solvents. Data are available only for a few systems and at limited conditions.

For more economical CO_2 capture and regeneration, there is a need for development of more efficient solvent systems. In this project we will extend the thermodynamic database by measuring heat of solution data of CO_2 in mixed solvents made of MEA (monoethanolamine), MDEA (methyldiethanolamine), piperazine, and water. Mixed solvents of different compositions will be selected and in each case data will be measured at a few temperatures and at different concentrations of the aqueous solutions. At the end of the project, observations, conclusions, and recommendations will be derived for the choice of mixed solvents for efficient CO_2 capture with potential for commercialization.

2. Progress of Experimental Measurements

All the data measured so far are summarized in Tables 1, 2, 3 and Figures 1 and 2. During the current period of performance, data measurements for CO_2 in aqueous mixtures of MDEA and piperazine were initiated and are currently continuing. The results of these measurements will be reported during the next reporting period. Some data measurements are also being attempted using an inorganic fluorinated salt as an additive. The intent is to investigate if this additive alters the solvent properties favorably. There was a delay in measurements caused because the graduate student performing the experiments quit due to personal reasons. A new M.S. student has

undertaken the measurements. Although it took over two months for this student to get familiar with the project, he has gained sufficient expertise to continue the measurements.

3. Data Analysis and Other Current Work

An observation our heat of solution data indicate that the heat of solution per mole of CO_2 is fairly constant with CO_2 loading at low CO_2 concentrations, but it decreases closer to the saturation concentration. Attempts are being made to model this behavior, and obtain expressions for heats of mixing as function of CO_2 concentration. The results will be presented when completed.

Some efforts are being made to extend the currently available thermodynamic models for these systems based on the electrolyte –NRTL/UNIQUAC activity coefficient correlations for enthalpy calculations. The approach involves development of EOS-G^E model with equations of state and mixing rules available in the literature.

4. Conclusions and Plans for the Next Quarter

In the next quarter, measurements with aqueous mixed solvents containing MDEA and piperazine will be completed, and some measurements with a fluorinated inorganic additive to aqueous MDEA solvent will be performed. The goal is to investigate if the additive alters the solvent properties favorably.

Table 1: Solubility and Enthalpy data for CO_2 in aqueous MDEA solvent

MDEA solution				
Temp ^0C	***Wt %***	***Solubility***	***kJ / mol CO_2***	***kJ / mol MDEA***
75				
	50	***0.708***	***-53.34***	***-37.89***
	30	***0.852***	***-52.47***	***-45.02***
	20	***0.911***	***-51.10***	***-45.94***
40				
	50	***1.083***	***-47.76***	***-51.78***
	30	***1.208***	***-43.45***	***-52.53***
	20	***1.269***	***-40.38***	***-51.27***
15				
	50	***1.220***	***-43.09***	***-52.39***
	30	***1.304***	***-39.27***	***-51.21***
	20	***1.341***	***-36.75***	***-49.27***

Table 2: Solubility and Enthalpy data for CO_2 in aqueous MEA solvent

MEA solution				
Temp ^0C	***Wt %***	***Solubility***	***kJ / mol CO_2***	***kJ / mol MEA***
75				
	50	***0.597***	***-76.99***	***-46.26***
	30	***0.711***	***-69.83***	***-49.76***
	15	***0.769***	***-67.32***	***-51.93***
40				
	50	***0.767***	***-65.63***	***-50.30***
	30	***0.878***	***-61.00***	***-52.06***
	15	***0.959***	***-59.72***	***-57.32***
15				
	50	***0.815***	***-65.31***	***-53.24***
	30	***0.912***	***-60.51***	***-55.18***
	15	***1.015***	***-57.44***	***-58.07***

Table 3: Solubility and Enthalpy data for CO_2 in aqueous MEA+MDEA mixed solvent

MEA + MDEA solution				
Temp ^0C	***MEA+MDEA Wt %***	***Solubility***	***kJ / mol CO_2***	***kJ / mol Amine***
75				
	24+6	***0.720***	***-73.39***	***-53.29***
	18+12	***0.753***	***-69.14***	***-51.99***
	6+24	***0.790***	***-61.89***	***-48.94***
40				
	24+6	***0.919***	***-60.54***	***-55.64***
	18+12	***0.971***	***-57.40***	***-55.74***
	6+24	***1.005***	***-53.71***	***-54.03***
15				
	24+6	***0.979***	***-52.06***	***-50.82***
	18+12	***1.084***	***-50.33***	***-54.60***
	6+24	***1.147***	***-45.39***	***-52.12***

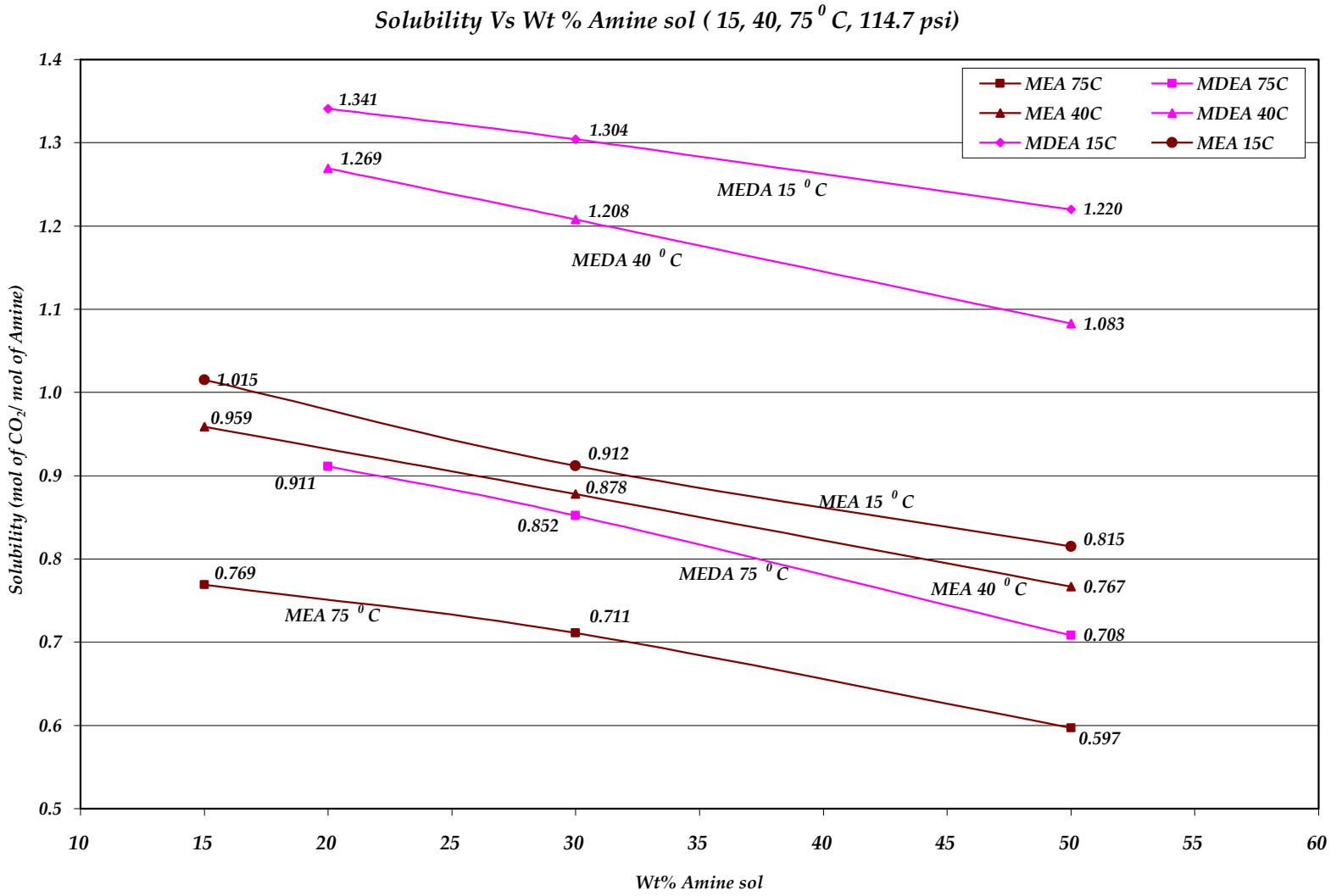

Figure 1: Solubility is plotted against wt% aqueous solution at various temperatures for MEA and MDEA solvents

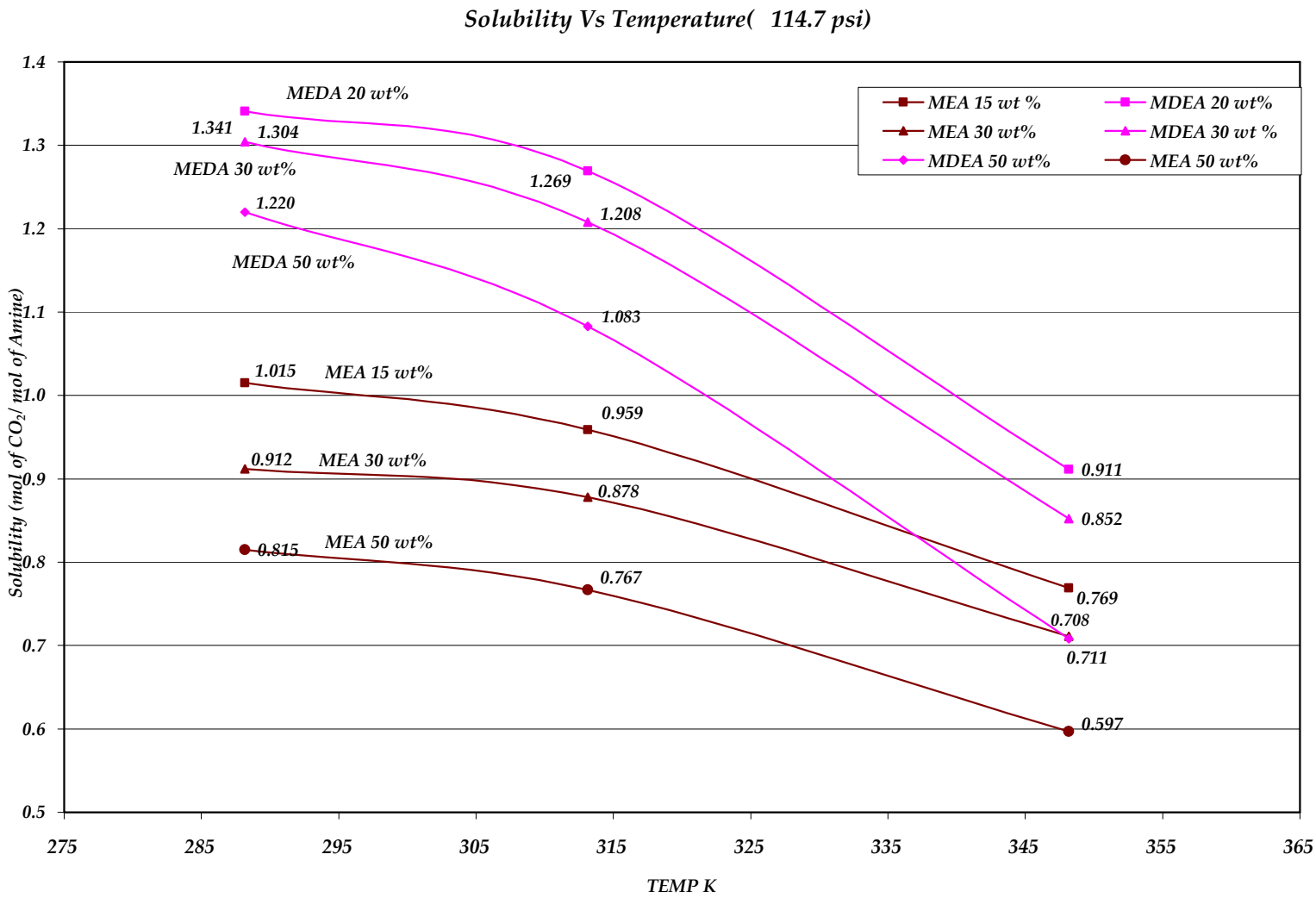

Figure 2: Solubility is plotted against temperature for various wt% of aqueous MEA and MDEA solvents